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## CLAIMS:

1. A controlled free radical polymerization process of atom or group transfer radical polymerization comprising the steps of:

5 polymerizing one or more radically (co)polymerizable monomers in the presence of a system initially comprising:

an initiator having one or more radically transferable atoms or groups,

a transition metal in its zero oxidation state which forms, in-situ, a first transition metal compound that participates in a reversible redox cycle with the initiator, a dormant polymer chain end, a growing polymer chain end or a mixture thereof, and

10 one or more N-, O-, P-, or S- containing ligands which coordinate in a  $\sigma$ -bond or a  $\pi$ -bond to the transition metal, or any C containing compound which can coordinate in a  $\pi$ -bond to the transition metal,

to form a (co)polymer.

2. The process of claim 1, wherein said polymerizing is performed in bulk, in  
15 solution, in suspension, in emulsion, in a supercritical fluid or in the gas phase.

3. The process of claim 1, further comprising isolating said (co)polymer.

4. The process of claim 1, wherein said system further comprises a second transition metal, which may be the same as or different from said first transition metal compound.

5. The process of claim 4, wherein said second transition metal compound  
20 participates in a reversible redox cycle with the initiator, a dormant polymer chain end, a growing polymer chain end or a mixture thereof.

6. The process of claim 5, wherein said second transition metal compound has a counterion that is different from said one or more radically transferable atoms or groups on said initiator.

25 7. The process of claim 5, wherein the one or more radically transferable atoms or groups on said initiator comprises bromine and wherein said second transition metal compound has a chlorine counterion.

8. The process of claim 1, wherein said initiator has an iodine as radically transferable atom or group.

9. The process of claim 5, wherein said transition metal compound has one or more counterions selected from the group consisting of non-radically transferable groups.

10. The process of claim 9, wherein said non-radically transferable group is a member selected from the group consisting of unsubstituted and substituted carboxylates, thophenecarboxylates, thiocyanates, triflates, phosphines, boranes,  $\text{PF}_6$ , hexafluorophosphate, nitrates, perchlorates, thiocarbamates, phosphates, sulfates, tosylates, acetylacetonate and cyanides.

11. The process of claim 1, wherein said one or more radically (co)polymerizable monomers is an  $\text{AB}^*$  monomer, wherein A is a carbon-carbon double bond and  $\text{B}^*$  is a functional group that can be transformed into an active site for initiating polymerization of carbon-carbon double bonds.

12. The process of claim 5, wherein said one or more radically (co)polymerizable monomers is an  $\text{AB}^*$  monomer, wherein A is a carbon-carbon double bond and  $\text{B}^*$  is a functional group that can be transformed into an active site for initiating polymerization of carbon-carbon double bonds.

13. The process of claim 4, wherein said second transition metal-compound comprises a metal that has at least two stable oxidation states, a higher oxidation state and a lower oxidation state, and wherein said metal is present in said higher oxidation state, such that upon reaction with said transition metal in a zero oxidation state, said metal of said second transition metal compound is reduced to the lower oxidation state to form a reduced metal conjugate of said second transition metal compound that participates in a reversible redox cycle with the initiator, a dormant polymer chain end, a growing polymer chain end or a mixture thereof.

14. The process of claim 13, wherein said higher oxidation state is the highest stable oxidation state available to said metal of said second transition metal-compound.

15. The process of claim 1, wherein the (co)polymer prepared has a degree of polymerization between 1 and 1,000,000.

16. The process of claim 1, wherein said transition metal in the zero oxidation state is a member selected from the group consisting of copper, iron, chromium, samarium, nickel,

manganese, silver, zinc, palladium, platinum, rhenium, rhodium, iridium, indium and ruthenium.

17. The process of claim 16, wherein said transition metal in the zero oxidation state is copper.

5 18. The process of claim 16, wherein said transition metal in the zero oxidation state is iron.

19. The process of claim 1, wherein said transition metal in the zero oxidation state is added in a form selected from the group consisting of a powder, a turning, a wire, a mesh, a film and an electrode.

10 20. The process of claim 1, wherein said system and said one or more radically (co)polymerizable monomers are not purified prior to addition to the process.

21. The process of claim 1, wherein said process is performed in the presence of air.

22. The process of claim 13, wherein there is a molar excess of said transition metal in the zero oxidation state relative to said second transition metal compound in the higher  
15 oxidation state lowers the concentration of the transition metal complex in the higher oxidation state such that said transition metal in the zero oxidation state lowers the concentration of the transition metal complex in the higher oxidation state and regenerates the reduced metal conjugate.

20 23. The process of claim 1, wherein the initiator is a monomeric initiator or a macromolecular initiator.

24. A controlled free radical polymerization process of atom or group transfer radical polymerization comprising the steps of:

polymerizing one or more radically (co)polymerizable monomers in the presence of a system initially comprising:

25 an initiator having one or more radically transferable atoms or groups,  
a transition metal compound having one or more associated counterions, wherein said transition metal compound participates in a reversible redox cycle with the initiator, a dormant polymer chain end, a growing polymer chain end or a mixture thereof, wherein said one or more associated counterions are different from said one or more radically  
30 (co)polymerizable monomers; and

one or more N-, O-, P-, or S- containing ligands which coordinate in a  $\sigma$ -bond or a  $\pi$ -bond to the transition metal, or any C containing compound which can coordinate in a  $\pi$ -bond to the transition metal,

to form a (co)polymer.

5        25. A process for coupling of one or more molecules, comprising:  
providing one or more molecules, each containing one or more radically transferable atoms or groups;

contacting said one or more molecules with a system comprising (a) at least a stoichiometric amount of a transition metal, relative to the total molar equivalents of said  
10 one or more radically transferable atoms or groups, wherein said transition metal is in an oxidation state that can participate in a redox reaction with the one or more radically transferable atoms or groups; and

one or more N-, O-, P-, or S- containing ligands which coordinate in a  $\sigma$ -bond or a  $\pi$ -bond to the transition metal, or any C containing compound which can coordinate in a  $\pi$ -  
15 bond to the transition metal;

to generate a free radical by transfer of the one or more radically transferable atoms or groups from the one or more molecules to the transition metal complex allowing coupling of the one or more molecules to occur.

26. The process of claim 25, wherein said one or more molecules is a first molecule  
20 having a single radically transferable atom or group, and wherein said coupling forms a second molecule having double the molecular weight of said first molecule after the molecular weight of said single radically transferable atom or group is subtracted from said molecular weight of said first molecule, and wherein said second molecule no longer contains the radically transferable atom or group.

25        27. The process of claim 25, wherein said one or more molecules is a molecule having two radically transferable atoms or groups and whereby said process provides chain extension of said molecule.

28. The process of claim 25, wherein said one or more molecules is a first molecule  $A-(X)_n$  having one or more radically transferable atoms or groups (X) and wherein said  
30 process further comprises a reactant molecule having radically reactive sites, such that upon

removal of said one or more radically transferable atoms or groups from said first molecule, the resulting radical reacts with said reactant molecule to form a compound  $A-(X)_{n-m}-(B)_m$  wherein B is the residue from the reactant molecule, n is the number of radically transferable atoms or groups and  $m \leq n$ .

5            29. The process of claim 28, wherein said reactant molecule is a hydrogen transfer agent.

30. The process of claim 29, wherein said hydrogen transfer agent is a member selected from the group consisting of thiols, silyl hydrides and tin hydrides.

31. The process of claim 28, wherein said reactant molecule is a stable free radical.

10           32. The process of claim 25, wherein said one or more molecules is a molecule having, on average, more than two radically transferable atoms or groups, and wherein the process produces a crosslinked compound containing units obtained from said molecule.

33. The process of claim 25, wherein said one or more molecules have, on average, at least two radically transferable atoms or groups and wherein said transition metal is  
15 contained at least on a surface of a substrate, such that upon contact of said surface with said one or more molecules a coherent coating is deposited on said surface.

34. The process of claim 25, wherein said transition metal is at least partially in a zero oxidation state.

20           35. The process of claim 34, wherein said transition metal is substantially completely in a zero oxidation state.

36. The process of claim 25, wherein said one or more molecules comprise a first molecule that is a polymer having a radically transferable atom or group at one or more termini and a second molecule having a radically transferable atom or group, wherein the product so formed is the polymer bound to said second molecule at each reactive termini  
25 with removal of both radically transferable atoms or groups.

37. The process of claim 36, wherein said second molecule is a bifunctional molecule having a radically transferable atom or group and a second functional group, such that upon coupling with each reactive terminus of the polymer and the second molecule, the resulting polymer product has the second functional group at the termini.

38. A controlled free radical polymerization process of atom or group transfer radical polymerization comprising the steps of:

polymerizing one or more radically (co)polymerizable monomers in the presence of a system initially comprising:

- 5           an initiator having one or more radically transferable atoms or groups,  
          a first transition metal-compound which participates in a reversible redox cycle with the initiator, a dormant/growing polymer chain end or both,  
          a second transition metal compound,  
          one or more N-, O-, P-, or S- containing ligands which coordinate in a  $\sigma$ -bond or a  
10           $\pi$ -bond to the first transition metal, or any C containing compound which can coordinate in a  $\pi$ -bond to the first transition metal,  
          to form a (co)polymer.

39. The process of claim 38, wherein said polymerizing is performed in bulk, in solution, in suspension, in emulsion, in a supercritical fluid or in the gas phase.

15           40. The process of claim 38, further comprising isolating said (co)polymer.

41. The process of claim 38, further comprising a third transition metal in its zero oxidation state.

42. The process of claim 38, wherein said second transition metal compound is in a redox conjugate oxidation state different from that of said first transition metal compound.

20           43. The process of claim 38, wherein said first and second transition metals are independently selected from the group consisting of copper, iron, manganese, magnesium, chromium, nickel, silver, palladium, ruthenium, samarium, zinc and rhodium.

44. A controlled free radical polymerization process of atom or group transfer radical polymerization comprising the steps of:

25           polymerizing one or more radically (co)polymerizable monomers in the presence of a system initially comprising:

- an initiator having one or more radically transferable atoms or groups,  
          a transition metal-compound having one or more associated counterions that are non-radically transferable, wherein the transition metal compound participates in a reversible  
30          redox cycle with the initiator, a dormant/growing polymer chain end or both,

one or more N-, O-, P-, or S- containing ligands which coordinate in a  $\sigma$ -bond or a  $\pi$ -bond to the transition metal, or any C containing compound which can coordinate in a  $\pi$ -bond to the transition metal,

to form a (co)polymer.

5        45. The process of claim 44, wherein the one or more ligands and counterions are chosen to form, along with the transition metal, a metal complex with monomeric structure when the transition metal is in a lower of at least two available oxidation states.

10       46. The process of claim 44, wherein the one or more ligands and counterions are chosen to form, along with the transition metal, a metal complex having more than one metal center.

47. A controlled free radical polymerization process of atom or group transfer radical polymerization for the preparation of (co)polymers comprising the steps of:

(a) initially polymerizing one or more radically (co)polymerizable monomers in the presence of a system comprising:

15       an initiator having one or more radically transferable atoms or groups,  
a transition metal-compound which participates in a reversible redox cycle with the initiator, a dormant/growing polymer chain end or both,

20       one or more N-, O-, P-, or S- containing ligands which coordinate in a  $\sigma$ -bond or a  $\pi$ -bond to the transition metal, or any C containing compound which can coordinate in a  $\pi$ -bond to the transition metal; to give a (co) polymer having a terminal radically transferable atom or group, wherein the terminal radically transferable atom or group may be the same as or different from the one or more radically transferable atoms or groups in the initiator; and

(b) converting the terminal radically transferable atom or group into an atom or group different from said terminal radically transferable atom or group.

25       48. The process of claim 47, wherein said atom or group is a third radically transferable atom or group, which may be the same as or different from the one or more radically transferable atoms or groups in said initiator.

30       49. The process of claim 47, further comprising (c) adding a second different radically (co)polymerizable monomer that adds to the terminus now bearing said third radically transferable atom or group, to provide a block copolymer.



50. The process of claim 47, further comprising (c) adding a second different radically (co)polymerizable monomer in an amount sufficient to cap the growing polymer chain ends and (d) subsequently adding a third radically (co)polymerizable monomer to provide a block copolymer having said second different monomer located between blocks.

5 51. The process of claim 50, wherein efficient polymerization of said third monomer will not occur with said one or more radically polymerizable (co)monomers under the reaction conditions without the presence of said second monomer between said blocks.

52. A controlled free radical polymerization process of atom or group transfer radical polymerization comprising the steps of:

10 polymerizing one or more radically (co)polymerizable monomers in the presence of a system initially comprising:

an initiator having one or more radically transferable atoms or groups,

a transition metal-compound that participates in a reversible redox cycle with the initiator, a dormant/growing polymer chain end or both, wherein the transition metal  
15 compound is, optionally, partially or completely present in a zero oxidation state, and

one or more ligands selected from the group consisting of phosphines, phosphites, quinolines, picolines and non-heteroaromatic amines;

to form a (co)polymer.

53. The process of claim 52, wherein said one or more ligands are selected from the  
20 group consisting of tri-n-butylamine, tri-n-octylamine and mixtures thereof, tertaalkylethylenediamine, quinolines, picolines, pentamethyldiethylenetriamine, hexamethyltriethylenetetraamine, 2-{{2-(dimethylamino)ethyl}-methylamino}ethanol, tris(2-(dimethylamino)ethyl)amine and cyclic non-heteroaromatic amines.

54. The process of claim 52, wherein said one or more ligands are selected from the  
25 group consisting of mono- and multidentate phosphines and mono- and multidentate phosphites.

55. A controlled free radical polymerization process of atom or group transfer radical polymerization comprising the steps of:

30 polymerizing one or more radically (co)polymerizable monomers in the presence of a system initially comprising:

an initiator having one or more radically transferable atoms or groups,  
a transition metal compound having at least one counterion associated therewith,  
wherein the transition metal compound participates in a reversible redox cycle with the  
initiator, a dormant polymer chain end, a growing polymer chain end or a mixture thereof,  
5 and

one or more N-, O-, P-, or S- containing ligands which coordinate in a  $\sigma$ -bond or a  
 $\pi$ -bond to the transition metal, or any C containing compound which can coordinate in a  $\pi$ -  
bond to the transition metal,

wherein said at least one counterion, said one or more ligands or both are chosen to  
10 adjust the transition metal compound's solubility, reactivity or both;  
to form a (co)polymer.

56. The process of claim 55, wherein said at least one counterion, said one or more  
ligands or both are chosen to allow separation of the transition metal compound from the  
(co)polymer formed in the process.

15 57. The process of claim 55, wherein said at least one counterion, said one or more  
ligands or both are changed into a different counterion, ligand or both after polymerization to  
allow separation of the transition metal compound from the (co)polymer formed in the  
process.

20 58. The process of claim 55, wherein said transition metal compound and said one or  
more ligands are present in a ratio of (transition metal compound):(total of said one or more  
ligands) from  $1:10^{-3}$  to  $1:10^3$ .

59. The process of claim 55, wherein said counterion and said ligand are one in the  
same.

25 60. The process of claim 55, further comprising a transition metal in a zero oxidation  
state.

61. The process of claim 55, wherein the polymerizing step is performed in bulk, in  
solution, in suspension, in an emulsion, in a supercritical fluid or in the gas phase.

30 62. The process of claim 55, wherein during said polymerization, the system is  
subjected to an applied electric potential to modify the redox potential of a transition metal  
complex formed from said transition metal compound and said one or more ligands.

63. A multifunctional polymerization initiator having at least one initiation site for atom or group transfer radical polymerization (ATRP) and at least one initiation site capable of initiating a non-ATRP polymerization.

5 64. The multifunctional polymerization initiator of claim 63, wherein said non-ATRP polymerization is a polymerization process selected from the group consisting of cationic, anionic, free radical, metathesis, ring opening and coordination polymerizations.

65. A process for the formation of a telechelic functional material, comprising:  
coupling two or more molecules, which may be the same or different, wherein each molecule has a radically transferable atom or group at one terminus and a non-radically transferable functional group at a second terminus, wherein the coupling is performed by  
10 reacting said two or more molecules in the presence of:

at least a stoichiometric amount of a zero oxidation state transition metal, relative to the molar amount of said radically transferable atom or group; and

one or more N-, O-, P-, or S- containing ligands which coordinate in a  $\sigma$ -bond or a  
15  $\pi$ -bond to the transition metal, or any C containing compound which can coordinate in a  $\pi$ -bond to the transition metal; then

isolating the telechelic functional material.

66. The process of claim 65, wherein said reacting of said two or more molecules is further performed in the presence of a transition metal compound which can participate in a reversible redox cycle with said radically transferable atom or group.  
20

67. A process for formation of telechelic polymers comprising:

polymerizing one or more radically (co)polymerizable monomers in the presence of a system initially comprising:

an initiator having one or more radically transferable atoms or groups,  
25 a transition metal compound that participates in a reversible redox cycle with the initiator, a dormant polymer chain end, a growing polymer chain end or a mixture thereof, and

one or more N-, O-, P-, or S- containing ligands which coordinate in a  $\sigma$ -bond or a  $\pi$ -bond to the transition metal, or any C containing compound which can coordinate in a  $\pi$ -  
30 bond to the transition metal,

to form a (co)polymer having a radically transferable atom or group at one terminus thereof; and

reacting said (co)polymer with at least one molar equivalent of said initiator, relative to the molar amount of said (co)polymer in the presence of at least a stoichiometric amount  
5 of a zero oxidation state transition metal to place an initiator residue at said one terminus in place of said radically transferable atom or group.

68. A polymerization process, comprising:

initiating a first polymerization of monomers using an initiator functionalized with an ATRP initiating site, wherein the first polymerization is selected from the group of cationic polymerization, anionic polymerization, conventional free radical polymerization, metathesis, ring opening polymerization, cationic ring opening polymerization, and coordination polymerization to form a macroinitiator comprising an ATRP initiating site; and

initiating an ATRP polymerization of radically polymerizable monomers using the macroinitiator comprising an ATRP initiating site.

69. The polymerization process of claim 68, wherein the first polymerization of monomers is a conventional radical polymerization and the initiator functionalized with an ATRP initiating site is at least one of functionalized azo compounds and peroxides.

70. The polymerization process of claim 68, wherein the first polymerization of monomers is a one of a cationic polymerization, anionic polymerization and a conventional radical polymerization and the initiator functionalized with an ATRP initiating site is a functionalized transfer agent.

71. The polymerization process of claim 68, wherein the first polymerization of monomers is a cationic ring opening polymerization and the initiator functionalized with an ATRP initiating site is one of a 2-halopropionyl halide/silver and 2-haloisobutyronyl halide/silver salt.

72. The polymerization process of claim 71, wherein the initiator functionalized with an ATRP initiating site is 2-bromopropionyl bromide/silver triflate.

73. The polymerization process of claim 68, wherein the first polymerization of monomers is one of a cationic polymerization and ring opening polymerization and the initiator functionalized with an ATRP initiating site is one of a 2-halopropionyl halide and 2-haloisobutyronyl halide.

74. The polymerization process of claim 73, wherein the initiator functionalized with an ATRP initiating site is 2-bromopropionyl bromide.

75. The polymerization process of claim 68, wherein the first polymerization of monomers is a conventional radical polymerization and the initiator functionalized with an ATRP initiating site is at least one of halogenated AIBN derivatives and halogenated peroxide derivatives.

76. The polymerization process of claim 68, wherein the first polymerization of monomers is an anionic polymerization and the initiator functionalized with an ATRP initiating site comprising hydroxy functionality.

77. The polymerization process of claim 76, wherein the initiator functionalized with an ATRP initiating site is 2-hydroxyethyl 2-bromopropionate.

78. A polymerization process, comprising:

initiating a first polymerization of monomers using an initiator, wherein the first polymerization is selected from the group of cationic polymerization, anionic polymerization, conventional free radical polymerization, metathesis, ring opening polymerization, cationic ring opening polymerization, and coordination polymerization to form a macromolecule;

quenching the first polymerization with a compound comprising an ATRP initiating site to form a macroinitiator comprising the macromolecule and an ATRP initiating site; and

initiating an ATRP polymerization using the macroinitiator comprising an ATRP initiating site.

79. The polymerization process of claim 78, wherein the first polymerization of monomers is a ring opening polymerization of cyclic hexamethylcyclotrisiloxane and the compound comprising an ATRP initiating site is 4-(chlorodimethylsilylethyl)styrene.

80. The polymerization process of claim 78, wherein the macromolecule is a polyphosphazene.